REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)

2. REPORT DATE
Sept. 2, 1996

3. REPORT TYPE AND DATES COVERED
Final 5/1/93 - 4/30/96

4. TITLE AND SUBTITLE
SYSTEMATIC OPTIMIZATION OF SECOND-ORDER NONLINEAR OPTICAL MATERIALS

5. FUNDING NUMBERS
F49620-93-1-0314
2303-CS
1651-01
61102F
63217C

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9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
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Dr. Charles Y-C Lee

AFOSR-TR-96
0462

11. SUPPLEMENTARY NOTES
approved for public release; distribution is unclassified.

12a. DISTRIBUTION / AVAILABILITY STATEMENT
Approved for public release;
distribution unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

Molecules that exhibit exceptionally large molecular nonlinearities have been identified. One of the molecules, when incorporated into a polycarbonate yield after electric field poling, has an electro-optic coefficient nearly twice that of lithium niobate when measured at a standard telecommunication wavelength. The molecules were based upon a heterocyclic acceptor with two strong electron withdrawing groups. This acceptor was examined in detail and the various molecules were synthesized to systematically study how chromophores incorporating this acceptor could be stabilized and why the acceptor was so effective relative to other extremely strong acceptors that were examined in the past.

In a parallel study, the use of diphenylaminothiophene as a donor for electro-optic materials was examined in some depth. This work was built upon work performed at IBM that demonstrated diphenylaminophenyl groups had improved thermal stability than dialkylamino phenyl groups. Given the understanding that in general compounds that contain amino thiophene groups as donors had higher nonlinearity than those containing aminophenyl groups, various diphenylamino thiophenes were synthesized and it was demonstrated that chromophores exhibiting high optical nonlinearities and excellent thermal stability could be synthesized in this manner.

19961016 122

DTIC QUALITY INSPECTED 4

15. NUMBER OF PAGES
16

16. PRICE CODE

OF REPORT
unclassified

18. SECURITY CLASSIFICATION OF THIS PAGE
unclassified

19. SECURITY CLASSIFICATION OF ABSTRACT
unclassified

20. LIMITATION OF ABSTRACT

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std Z39-18
298-102

FINAL REPORT FOR: SYSTEMATIC OPTIMIZATION OF SECOND-ORDER NONLINEAR OPTICAL MATERIALS

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AFOSR GRANT # F49620-93-1-0314

2. OBJECTIVES

The objectives of this work are to 1) develop a fundamental understanding of the chemistry that will lead to thermally, electrochemically, and photochemically stable second-order nonlinear optical materials and 2) to develop advanced electrooptic and photonic materials for enhanced performance of optoelectronic interconnects and optical computing systems.

3. STATUS OF EFFORT

Molecules that exhibit exceptionally large molecular nonlinearities have been identified. One of the molecules, when incorporated into a polycarbonate yield after electric field poling, has an electro-optic coefficient nearly twice that of lithium niobate when measured at a standard telecommunication wavelength. The molecules were based upon a heterocyclic acceptor with two strong electron withdrawing groups. This acceptor was examined in detail and the various molecules were synthesized to systematically study how chromphores incorporating this acceptor could be stabilized and why the acceptor was so effective relative to other extremely strong acceptors that were examined in the past.

In a parallel study, the use of diphenylaminothiophene as a donor for electro-optic materials was examined in some depth. This work was built upon work performed at IBM that demonstrated diphenylaminophenyl groups had improved thermal stability than dialkylamino phenyl groups. Given the understanding that in general compounds that contain amino thiophene groups as donors had higher nonlinearity than those containing aminophenyl groups, various diphenylamino thiophenes were synthesized and it was demonstrated that chromophores exhibiting high optical nonlinearities and excellent thermal stability could be synthesized in this manner.

4. ACCOMPLISHMENTS/NEW FINDINGS

The goal of this section is not to provide an exhaustive compilation of data that is largely published or submitted, but rather to show how the series of studies has provided a direction towards materials with large optical nonlinearities, excellent thermal stability, and reasonable transparency. Many of these goals were met, and the paragraphs below will show molecules are now available, which if incorporated into polymers at loading levels of 30% by weight, and were poled a 100V/μm, would yield thermal stable polymers with electro-optic coefficients. The

current challenge is now to fulfill these last set of criteria. However, the studies performed to date provide a knowledge base such that these goals appear obtainable.

4.1 Optimization of Molecules and Polymeric Optical Nonlinearities

The high degree of bond length alternation observed in the central polyene bridge of donor-acceptor substituted stilbenes and related molecules was shown to be indicative of an insufficient contribution of the charge-separated resonance form to the ground-state configuration of the molecules to lead to extremely large β. It was believed that this was a consequence of the loss of aromatic stabilization in the charge-separated form. Therefore, donor-acceptor polyenes were designed wherein the loss of aromaticity in one end upon charge-separation (in the case the donor end) would be somewhat offset by a gain in aromaticity upon charge-separation in the opposite end. It was predicted that such molecules would have more nearly the correct contribution of the charge-separated form to the ground-state structure required to reach the bond length alternation at which β is maximized.

Compounds with acceptors that can gain aromaticity in their charge-separated resonance forms, such as $(CH_3)_2NC_6H_4$-$(CH{=}CH)_n$-A and julolidinyl-$(CH{=}CH)_n$- A, where A is, N, N'-diethylthiobarbituric acid, or 3-phenyl-5-isoxazolone for n = 0-3, were synthesized and had large β values and reduced $\langle\Delta r\rangle$ in comparison with compounds where A = $C_6H_4NO_2$. It was expected that the potential gain in aromaticity upon charge separation would lead to a substantial charge transfer and reduced bond length alternation in the ground state. Thus, molecules containing acceptors whose topology dictates that aromaticity is gained upon charge separation (such as 3-phenyl-5-isoxazolone or N, N'-diethyl-thiobarbituric acid) would have more nearly the correct degree of bond length alternation needed to optimize β and could thus give rise to extremely large optical nonlinearities compared to conventional molecules of similar length.

Hyperpolarizabilities were measured by electric field induced second harmonic generation (EFISH) in chloroform, with 1.907 μm fundamental radiation. The values of β thus obtained support the hypothesis that molecules of only moderate lengths containing the 3-phenyl-5-isoxazolone or N,N'-diethyl-thiobarbituric acid acceptor can have unprecedented β values The dispersion-corrected β(0) and μβ(0) values of the n = 0 and 1 compounds, which are analogous to ones previously reported, are not exceptional in comparison to other molecules in the literature. However, the longer n = 2 and 3 vinylogs exhibit strikingly large β(0) and μβ(0) values for their lengths. The importance of the topology of the π system is clearly illustrated if one considers that both $(CH_3)_2NC_6H_4$-CH=CH-C_6H_4CHO, and julolidinyl-$(CH{=}CH)_2$-CH=N, N'-diethylthiobarbituric acid, have ten conjugated atoms between the amine donor to the carbonyl

acceptor, yet the former has a $\beta(0)$ of 20 x 10^{-30} esu, whereas the latter compound has $\beta(0)$ of 490 x 10^{-30} esu.

Pursuant to this study, a series of chromophores based on a very strong acceptor [3-(dicyanomethylidene)-2,3-dihydrobenzothiophen-2-ylidene-1,1-dioxide] which contains two strong electron withdrawing groups, the dicyanomethylidene and the sulfone group, were synthesized. In particular, (4-N,N-di-*n* butylamino)phenyl-$(CH{=}CH)_2$-3-(dicyanomethylidyl)-2,3-dihydrobenzothiophene-1,1-dioxide and had a $\mu\beta > 10{,}000 \times 10^{-48}$ esu were used.

In an attempt to determine if the large molecular nonlinearities in (4-N,N-di-*n* butylamino)phenyl-$(CH{=}CH)_2$-3-(dicyanomethylidyl)-2,3-dihydrobenzothiophene-1,1-dioxide would lead to a large electro-optic coefficient in a poled polymer, it was incorporated into polycarbonate thin films at a reasonably high concentration for poled polymer studies. Thus a polycarbonate (PC) film containing 20 weight percent of (4-N,N-di-*n* butylamino)phenyl-$(CH{=}CH)_2$-3-(dicyanomethylidyl)-2,3-dihydrobenzothiophene-1,1-dioxide was spin coated onto an indium tin oxide coated glass substrate and a thin film of gold was deposited on top of the polymer as the second electrode. The chromophore-PC composite was poled at 80°C with an applied field of 150 V/μm. After cooling the sample to ambient temperature, the electro-optic coefficient was determined at 1.313 μm with modulated ellipsometry. The poled chromophore PC-composite yielded an r_{33} value of 55 pm/V, substantially greater than previously reported values for poled polymers .

A polymer sample kept at room temperature retained 85% of the initial value of the electro-optic coefficient 100 hours after poling, and gave the same value after 300 hours, demonstrating good thermal stability at room temperature. However, we expect that the low glass transition temperature T_g of the polymer (~ 80°C) will preclude its use in commercial devices. It would be necessary to use a polymer with a significantly higher T_g to improve the long-term temporal stability of the poling induced alignment of the chromophore, and thus the chromophore itself must be sufficiently stable to survive the poling and processing conditions above T_g. Examination of the absorption spectrum of (4-N,N-di-*n* butylamino)phenyl-$(CH{=}CH)_2$-3-(dicyanomethylidyl)-2,3-dihydrobenzothiophene-1,1-dioxide before and after heating in methylnapthalene (an inert high boiling solvent) at 150°C in air indicated that after 20 min. (adequate time for the poling procedure) there was significant (~40%) decomposition of the chromophore. We have found that substitution of thiophene for an olefinic double bond in the π-electron bridge could lead to significant improvement in thermal stability of the chromophore without a dramatic sacrifice in its optical nonlinearity. Accordingly, a new thiophene analog in which one of the double bonds in the polyene bridge was replaced by a thiophene ring, by a reaction analogous to that used for (4-N,N-di-*n* butylamino)phenyl-$(CH{=}CH)_2$-3-

(dicyanomethylidyl)-2,3-dihydrobenzothiophene-1,1-dioxide was synthesized. The new compound retained the excellent solubility observed for (4-N,N-di-*n* butylamino)phenyl-$(CH=CH)_2$-3-(dicyanomethylidyl)-2,3-dihydrobenzothiophene-1,1-dioxide and was somewhat more nonlinear than (4-N,N-di-*n* butylamino)phenyl-$(CH=CH)_2$-3-(dicyanomethylidyl)-2,3-dihydrobenzothiophene-1,1-dioxide, despite having improved optical transparency. In addition, the new thiophene-containing compound showed no significant decomposition after heating in methylnaphthalene at 150°C for 20 min. (less than 5%) and less than 10% decomposition after heating at 200°C for 20 min. Thus, these results suggest that it is possible to develop chromophores with high optical nonlinearity and adequate thermal stability and to permit incorporation into high-T_g polymers.

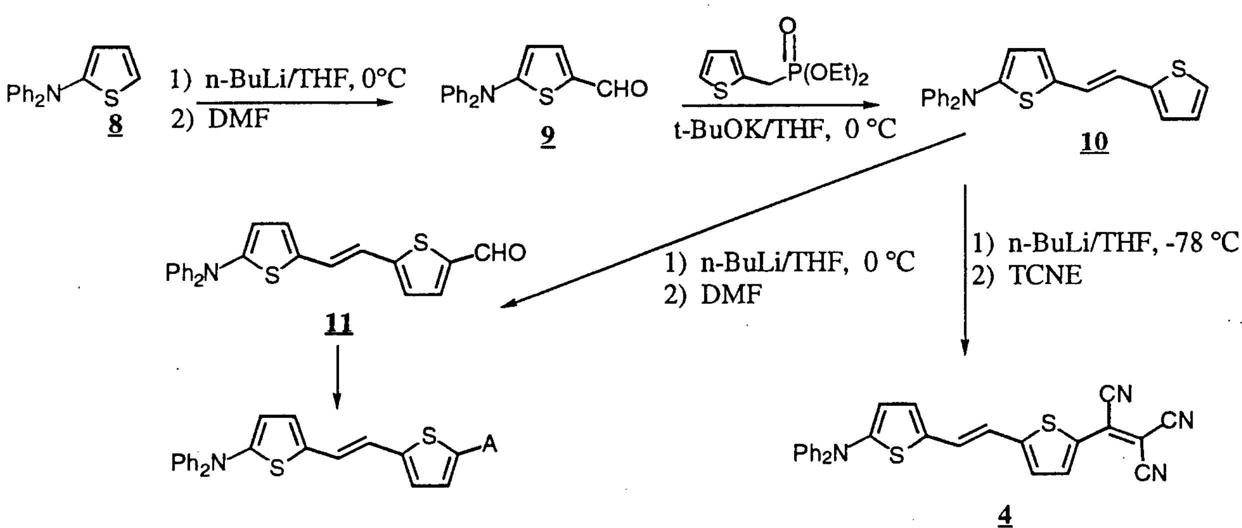
The results described above suggest that the [3-(dicyanomethylidene)-2,3-dihydrobenzothiophen-2-ylidene-1,1-dioxide] acceptor is sufficiently powerful to lead to very large $\mu\beta$ for several extended di-alkylaminophenyl substituted chromophores. In addition, the r_{33} value reported here is significantly larger than any value that has been reported to date for a poled polymer and almost twice that of lithium niobate. Molecules can be synthesized that have not only large nonlinearities but also reasonable stability at 200°C. Although much additional work must be done before commercially viable electro-optic polymers with such large r_{33} values become available, these results validate the concept that organic polymers can have substantially larger optical nonlinearities than lithium niobate.

4.2 Improving Thermal Stability Without Sacrifice of Nonlinearity

In poled E-O polymer systems, the alignment of the polar order can be preserved either by using host polymers with high glass transition temperatures (200-300 °C), or by cross-linking the chromophore-polymer composite. In either case, it poses a challenge for chemists in this field to develop highly nonlinear chromophores with thermal stabilities exceeding 250 °C in order to survive the material processing and device fabrication conditions. Recently, it has been shown that very large nonlinearities can be achieved by employing thiophene rings as conjugating units since they have lower aromatic stabilization energy upon charge separation than do benzene rings. Also, several reports from the literature have demonstrated that very high thermal stability of the chromophores can be imparted by using a diphenylamino functional group to replace a dialkylamino functional group as an electron-donor. However, due to the difficulty in functionalizing a thiophene ring with a diphenylamino donor, very little information has been reported on nonlinear optical chromophores that combine the advantages of using thiophene conjugating moiety and a diphenylamino electron-donor. Accordingly, a series of highly

nonlinear and thermally stable diphenylamino substituted thiophene stilbenes were synthesized and characterized. One of these chromophores was incorporated into a high Tg (265 °C) polyquinoline to form a composite that after electric field poling exhibited high E-O coefficients and good temporal stability.

The syntheses of compounds **1-3** in **Table 1** have been described previously and are listed for comparison. 2-(N,N-diphenylamino)thiophene **8** was obtained using a modified Ullman coupling reaction of 2-iodothiophene and potassium diphenylamine in polar aprotic solvents such as dimethylpropyleneurea (DMPU) or hexamethylphosphoramide (HMPA). The diphenylaminothiophene **8** was then lithiated with n-butyllithium (n-BuLi) and converted to 2-N,N-diphenylamino-5-thiophenecarboxaldehyde **9**. The diphenylamino substituted thiophene stilbene **10** was obtained by the Wittig-Horner condensation reaction of carboxaldehyde **9** with diethyl-2-thiophenemethylene phosphonate. Lithiation of **10** with n-BuLi and subsequent quenching with N,N-dimethylformamide (DMF) or tetracyanoethylene (TCNE) results in the corresponding aldehyde **11** and tricyanovinyl substituted compound **4**. Treatment of aldehyde **11** with malononitrile, diethylthiobarbituric acid, and 3-dicyanomethylidinylindane-1-one gave compounds **5-7** in 70-80% yield.



A= dicyanovinyl, 5

2-methylidene-3-dicyanomethylidinylindane-1-one, 6

4-methylidenediethylthiobarbituric acid, 7

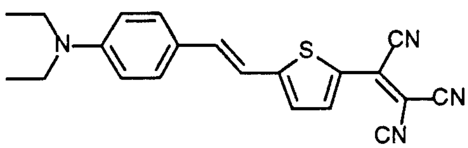
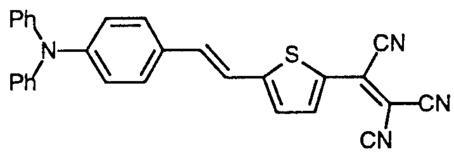
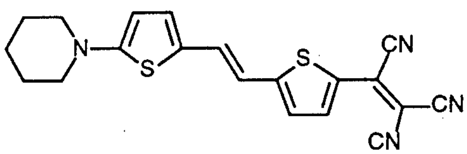
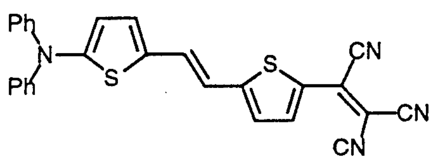
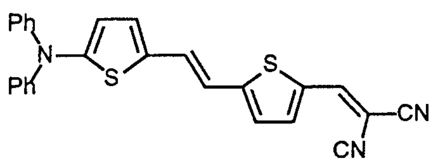
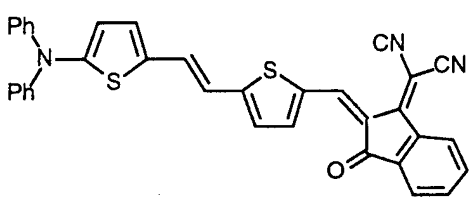
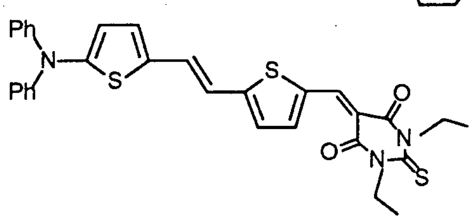
Scheme

Second-order hyperpolarizabilities of compounds **1-7** were determined using an EFISH. To minimize possible resonance enhancement which would exaggerate the measured nonlinear

responses, measurements were performed at a fundamental wavelength of 1907 nm. **Table 1** summarizes the electronic absorption and nonlinear optical properties of these compounds. Comparison of the $\beta\mu$ values (the scalar product of the vectorial component of the first hyperpolarizability tensor and the dipole moment) obtained for compounds **1-4** revealed significant blue shifted charge-transfer absorption (39-53 nm) upon changing the electron donor from the dialkylamino to diphenylamino functional group. However, the $\beta\mu$ value of compound **4** was surprisingly found to be 50% higher than that of compound **3**, while the $\beta\mu$ value of the compound **2** was half of its analog compound **1**. This phenomenon may be explained in terms of the relationship between β and the extent of ground-state polarization in the molecule, as is summarized below. It has been shown that β, as a function of ground-state polarization, (or degree of bond length alternation) has low values for molecules with relatively low polarization. It then increases with increasing donor and acceptor strength, reaches a positive peak, and then decreases to zero when half of the charge is transferred from the donor to the acceptor. Further polarization leads to negative values of β. **Figure 1** illustrates this relationship between β and bond length alternation as well as the various dependencies of the variables that contribute to β within the two-level approximation wherein:

$$\beta \propto \left(\mu_{ee}-\mu_{gg}\right)\left(\frac{\mu_{ge}^2}{E_{ge}^2}\right) \qquad (1)$$

Table 1

	Compound	λ_{max} (nm) in dioxane	βμ (10^{-48} esu) at 1907 nm	Td/°C
1		640	6200	240
2		601	3250	315
3		718	6900	200
4		665	10200	265
5		540	1280	325
6		641	4130	270
7		585	1800	235

where g is the index of the ground state, e is the index of the charge-transfer excited state, and μ is the dipole matrix element between the two subscripted states. In the context of this model, the unusual trends for compounds **1-4** can be explained as follows: It is believed the diphenylamino donor acts as a weaker donor than the dialkylamino donor in the ground-state. Accordingly, the compounds with the diphenylamino donors are closer to the polyene limit than their corresponding dialkylamino donors. Furthermore, since the thiophene-vinylene-thiophene bridge between the donor and acceptor allows for relatively efficient charge separation in the ground-state and since tricyanovinyl is a very potent acceptor, it is possible to have a large degree of ground-state polarization in the thiophene chromophores. As a result, one can hypothesize that compounds **1** and **2** are on the rising side of the β vs. the bond length alternation curve (Figure 1, extreme left), compound **3** is sufficiently polarized that it is on the falling side of the curve (Figure 1, somewhat left of center). Thus, whereas in most cases that have been previously examined, substitution of the thiophene ring on the donor end of the molecule for a phenyl ring leads to a substantial decrease in $\beta\mu$, for compound **1** vs. **3** this substitution results in only a ~10% decrease in $\beta\mu$, despite the fact that compound **1** is blue shifted by 78 nm relative to compound **3**. Accordingly, it is reasonable to propose that **3** is somewhat past the positive peak in β curve, and thus replacement of the dialkylamino donor with the weaker diphenylamino donor should not only lead to an increase in β and $\beta\mu$ (Figure 1) but should also lead to a significant blue shift of the absorption maxima (see predicted dependence of $1/E_{ge}^2$ in Figure 1), as was observed. Thus, the preceding explanation explains all the unusual results in a completely self consistent manner. Definitive verification of the hypothesis will require further studies such as solvent dependent measurements of β or the change in dipole moment between the ground state and the charge-transfer excited state.

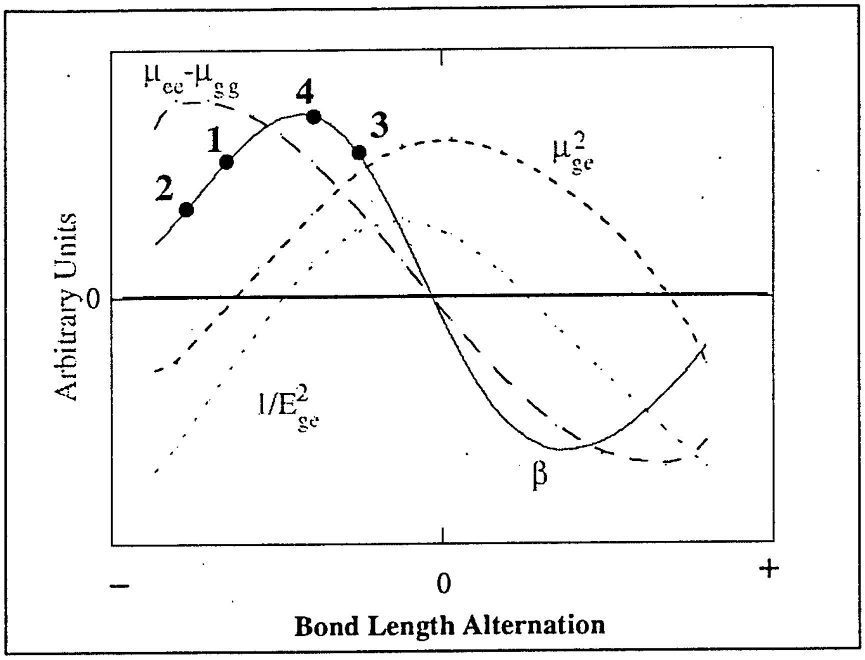


Figure 1. The calculated dependence of the ground-state structure on μ^2_{ge} (- - - -), $1/E^2_{ge}$ (····), μ_{ee} - μ_{gg} (– – – –) and β (———) in arbitrary units for $(CH_3)_2N$-$(CH=CH)_4$-CHO in the presence of an electric field used to tune the geometry, showing the hypothesized positions of **1-4** on the β curve.

The inherent thermal stabilities of these diphenylamino substituted stilbenes were determined by differential scanning calorimetry (DSC). Each of the samples was heated in a sealed pan at a rate of 20 °C/min. to give a Tm (melting point) and Td (onset of decomposition temperature). The diphenylamino substituted compounds **2** and **4-6** were shown to possess high thermal stability in the range of 250-325 °C, which makes them ideal candidates for the incorporation into high temperature polymers for device applications. However, compound **7** had a relatively low decomposition temperature (235 °C); this instability may have been due to the thermal oxidation of the methylidenediethylthiobarbituric acid electron acceptor. Among the compounds listed in **Table 1**, compound **4**, in particular, possessed both very high βμ value (10,200 x 10^{-48} esu) and good thermal stability up to 265 °C, which is a significant improvement over its dialkylamino analog **3** that has a lower βμ value (6900 x 10^{-48} esu) and a lower thermal decomposition temperature (200 °C).

Electro-optic studies were performed by doping compound **4** (15 wt %) into a high temperature polyquinoline (PQ-100 from Maxdem, Tg = 265 °C). Optical quality thin films (2-3 μm) were obtained by spin-coating a 15 % m/m solution (filtered through 0.2 μm syringe filter) of the resin in cyclopentanone. The films were kept in a vacuum oven at 120 °C for 24 h and briefly heated in a hot stage at 180 °C (N_2) for 20 min. to ensure removal of the residual solvent. A thin layer of gold was vacuum sputtered onto the polyquinoline films to serve as the top electrode for poling. The samples were poled at 180 °C with an applied dc electric field of 0.5 $MVcm^{-1}$, cooled to room temperature, and the poling field was subsequently removed. The E-O activity of the poled polymer film was measured at a wavelength of 1.3 μm with an experimental setup similar to that described by Teng and Mann, and an electro-optic coefficient (r_{33}) value of 12.6 pmV^{-1} was obtained. The thermal stability of the poled polymer was demonstrated by heating the poled sample in an oven at 80 °C for over 500h. The E-O activity of the sample shows an initial drop to 85% of its original value within 10 h; and then it remains unchanged during this period of time.

In conclusion, this work has led to a series of highly efficient and thermally stable chromophores. The incorporation of these chromophores into a high T_g polyquinoline yielded a polymer with high E-O coefficients and good temporal stability.

5. PERSONNEL SUPPORTED

Postdoctoral fellows who were supported either directly by salary or support for laboratory expenses are:

Peter Bedworth

Chin-Ti Chen

Sandra Gilmour (National Research Council Resident Research Associate, no salary support, laboratory expenses only)

Christopher Gorman (Jet Propulsion Laboratory Postdoctoral Fellowship, no salary support, laboratory expenses only)

Zhongying Hu

Dennis Ng

Rafeal Ortiz

Zhe Wu

Others supported by grant:

Erica Liang (High School Student)

Lael Erskine (Caltech Undergraduate Student)

In addition, several people who are not directly receiving funding from this grant but who are performing work in a collaborative manner include:

Dr. Grant Bourhill (Jet Propulsion Laboratory)

Dr. Larry Dalton (University of Southern California)

Dr. Alex Jen (EniChem)

Dr. Fabienne Meyers (Visiting Scientist from the University of Mons, Belgium)

Dr. Bob Montgomery (Visiting Scientist from the University of Southern California)

Dr. Joseph Perry (Jet Propulsion Laboratory)

6. PUBLICATIONS

1. Marder S.R.; Cheng, L.-T.; Tiemann, B.G.; Friedli, A.C.; Blanchard-Desce, M.; Perry, J. W.; Skindhøj, J. "*Large First Hyperpolarizabilities in Push-Pull Polyenes by Tuning Bond Length Alternation and Aromaticity.*" Science, **263** 511 (1994).

2. Gilmour, S; Jen, A.; Marder, S. R.; Niessink, A. J.; Perry, J. W.; Skindhøj, J.; Cai, M. " *Second-order Nonlinear Optical Properties of Thiophene Containing Chromophores with Extended Conjugation* ." in Materials Research Society Symposium Proceedings Vol. 328, Garito, A. F.; Jen, A.K.-Y.; Lee, Y.-C.; Dalton, L. R. eds, Materials Research Society, Pittsburgh, 1994. p. 485

3. Gilmour, S; Marder, S. R.; Perry, J. W.; Cheng, L.-T. "*Large Second-Order Optical Nonlinearities and Enhanced Thermal Stabilities in Extended Thiophene Containing Compounds.*" Adv. Mater., **6**, 494 (1994).

4. Gilmour, S; Montgomery, R. A. Marder, S. R.; Cheng, L.-T. Jen, A. K.-Y.; Cai, Y. M.; Perry, J. W.; Dalton, L. R. "*Synthesis of Diarylthiobarbituric Acid Chromophore with Enhance Second-Order Optical Nonlinearities and Thermal Stability.*" Chem. Mater., **6**, 1603 (1994).

5. Marder S.R.; Cheng, L.-T.; Tiemann, B.G.; Friedli, A.C.; Blanchard-Desce, M.; Perry, J. W.; Skindhøj, J. "*Large First Hyperpolarizabilities in Push-Pull Polyenes by Tuning Bond Length Alternation and Aromaticity.*" Science, **263** 511 (1994).

6. Gilmour, S; Jen, A.; Marder, S. R.; Niessink, A. J.; Perry, J. W.; Skindhøj, J.; Cai, M. " *Second-order Nonlinear Optical Properties of Thiophene Containing Chromophores with Extended Conjugation* ." in Materials Research Society Symposium Proceedings Vol. 328, Garito, A. F.; Jen, A.K.-Y.; Lee, Y.-C.; Dalton, L. R. eds, Materials Research Society, Pittsburgh, 1994. p. 485

7. Gilmour, S.; Marder, S.R.; Perry, J.W; Cheng, L.-T.; "*Enhanced Second-Order Nonlinearities in Extended Thiophene Containing Compounds.*" Proc. SPIE, **2143**, 117 (1994).

8. Ortiz, R.; Marder, S.R. Cheng, L.-T. Tiemann, B.G. Cavagnero, S.; Ziller, J.W. "*The Dependence of the Molecular First Hyperpolarizabilities of Merocyanines on Ground-State Polarization and Length.*" J. Chem. Soc., Chem. Commun., 2263 (1994).

9. Marder S. R.; Cheng, L.-T.; Tiemann, B. G.; Friedli, A. C.; Yang, E. "*Large First Hyperpolarizabilities in Push-Pull Polyenes with Strong Acceptors.* " Nonlinear Optics, **9**, 213 (1995).

10. Alhleim, M; Barzoukas, M; Bedworth, P. V.; Blanchard-Desce, M.; Fort, A.; Marder, S. R.; Perry, J. W.; Runser, C.; Stähelin, M; Zysset, B. "*A New Chromophore Doped Polymer with a Large Electro-Optic Coefficient.*" Science, **7**, 215 (1996).

11. Stähelin, M; Alhleim, M; Zysset, B.; Marder, S. R.; Barzoukas, M; Fort, A. "*Nonlinear Optical Properties of Novel Push-Pull Polyenes for Electro-optics.*" J. Op. Soc. Am. B., accepted for publication.

12. Friedli, A. C.; Yang, E.; Marder, S. R. "*A Convenient Synthesis of Polyenals with Extended Conjugation.*" Tetrahedron, accepted for publication.

7. INTERACTIONS

7.1 Papers presented at scientific conferences

1. Marder, S.R. "*Relationships Between Linear and Nonlinear Polarizabilities and Bond Length Alternation in Organic Molecules.*" Presented at the Canadian Chemical Society Nation Meeting, Sherbrooke, Quebec, Canada, May 30-June 4, 1993. (Invited Lecture).

2. Bourhill, G.H.; Brédas, J.L.; Cheng, L.-T.; Friedli, A.C.; Gorman, C. B.; Marder, S.R.; Meyers, F.; Perry, J.W.; Pierce, B.M.; Skindhøj, J.; Tiemann, B.G. "*Optimizing the First and Second Hyperpolarizabilities of Organic Dyes*" Presented at, Optical Society of America Topical Meeting: Organic Thin Films for Photonic Applications, Toronto, Canada, October 6-8, 1993. (Invited Lecture).

3. Marder, S.R. "*Attempts to Understand Relationships Between Chemical Structure and the Second- and Third-Order Optical Nonlinearities of Organic Molecules and Materials.*" Presented The First NSF-Sponsored Materials Chemistry Workshop, Albuquerque, NM, October 21-24, 1993.

4. Marder, S.R. ; Tiemann, B.G.; Perry, J.W.; Bourhill, G.H.; Gorman, C.B.; Friedli, A.C.; Cheng, L.-T.; Meyers, F.; Brédas, J.L.; Pierce, B.M. "*Structure Property Relationships for Second- and Third-Order Nonlinear Optics.*" Presented at Materials Research Society National Meeting, Boston, MA, November 29-December 3, 1993.(Invited Lecture).

5. Cheng, L.-T. Friedli, A.C.; Gilmour, S.; Gorman, C. B.; Marder, S.R.; Perry, J.W.; Perry, K. J.; Skindhøj, J.; Tiemann, B. G., Yang, E. "*The Effect of Bond Length Alternation on The Molecular Hyperpolarizabilities of Polymethine Dyes*" Presented at, The International Conference on Organic Nonlinear Optics, Val Thorens, France, January 9-13, 1994.

6. Bourhill, G.H.; Cheng, L.-T.; Gorman, C. B.; Marder, S.R.; Perry, J.W.; Tiemann, B.G. "*Hyperpolarizabilities of Conjugated Donor-Acceptor Molecules with Varying Degree of Charge-Transfer in the Ground-State.*" Presented at, The International Conference on Organic Nonlinear Optics, Val Thorens, France, January 9-13, 1994.

7. Marder, S.R." *A Chemists View of the Science and Technology of Organic Nonlinear Optical Materials.*" Presented at the American Chemical Society National Meeting, San Diego, CA, March 13-18, 1994.

8. Marder, S.R." *Designing Highly Nonlinear Organic Dyes* " Presented at the Fourth Iketani Conference, The International Conference on Optical Nonlinear Organic Materials and Applications, Kona, HI, May 17-20, 1994.

9. Marder, S.R." *The Relationship Between Ground-State Polarization and Molecular Polarizability and Hyperpolarizabilities of Organic Dyes* " Presented at the Gordon Conference on Electronic Properties of the Organic Solid State, Andover, NH, July 24- 29, 1994.

10. Marder, S.R." *Simple Models for Nonlinear Polarization in Organic Dyes* " Presented at the Fifth Annual Symposium of the NSF Center for Photo-induced Charge Transfer, Rochester, NY, August 1-3, 1994.

11. Marder, S.R. "*Nonlinear Optical Properties of Organic Dyes* " Presented at the Gordon Conference on Electron Donor-Acceptor Interactions, Salve Regina, RI, August 14-19, 1994.

12. Marder, S.R." *Optimizing Molecular Hyperpolarizabilities in Linear Conjugated Organic Molecules* " Presented at joint American Chemical Society, Optical Society of America Topical Meeting: Organic Thin Films for Photonic Applications, Washington, DC, August 22-26, 1994.

13. Marder, S. R. "*Attempts to Understand and Control the Nonlinear Optical Properties of Polymethine Dyes.* " Presented at Advanced Materials for Molecular Electronics and Photonics, Mons, Belgium, December 1-2, 1994.

14. Marder, S.R." *Design of Chromophores for Second-Order Nonlinear Optical Applications*" Presented at American Chemical Society National Meeting, Anaheim, CA, April, 2-7, 1995.

15. Marder, S. R. (Presented by Fabienne Meyers)" *Rational Design of Nonlinear Optical Materials*" Presented at The Royal Society of Chemistry's Second International Meeting on Materials Chemistry, Kent, England, July, 18-21, 1995. (Plenary Lecture)

16. Marder, S.R. (Presented by Rafael Ortiz) "*Design of Highly Nonlinear Chromophores for Electro-optic Applications*" Presented at the International Conference on Advanced Materials, Sponsored by the International Research Society, Cancun, Mexico, August 27-30, 1995.

17. Marder, S.R."*Design of Chromophores for Electro-optic Applications*" Presented at Optical Society of America/American Chemical Society Joint Topical Meeting: Organic Thin Films for Photonic Applications, Portland, OR, September 11-14, 1995.

18. Marder, S.R."*Materials for Electro-optic Applications*" Presented at Materials Research Society National Meeting, Boston, MA, November 27-December 1, 1995.

19. Marder, S.R. "*Organometallic Chromophores for Nonlinear Optical Applications.*" Presented at The American Chemical Society National Meeting, New Orleans, LA, March 24-28, 1996.

7.2 Consultive and advisory functions to other laboratories

1. Advice is provided on an ad hoc basis to the China Lake Naval Weapons Center and AFOSR.

7.3 Transitions

1. Our work on heterocyclic chromophores is being done in close collaboration with ROITechnologies, in particular with Alex Jen. Several of our systems are being incorporated into polymer systems for further investigation as electro-optic materials.

8. NEW DISCOVERIES INVENTIONS OR PATENT DISCLOSURES

1. Staehelin, M.; Ahlheim, M.; Zysset, B.; Marder, S.R. "*Polymethin Chromophores with Nonlinear Optical Properties*." German Priority Patent Application, Filed July 1994.

9. HONORS/AWARDS

1. Seth Marder, Elected to Board of Editors of *Science*.